UCB009-CHEMISTRY

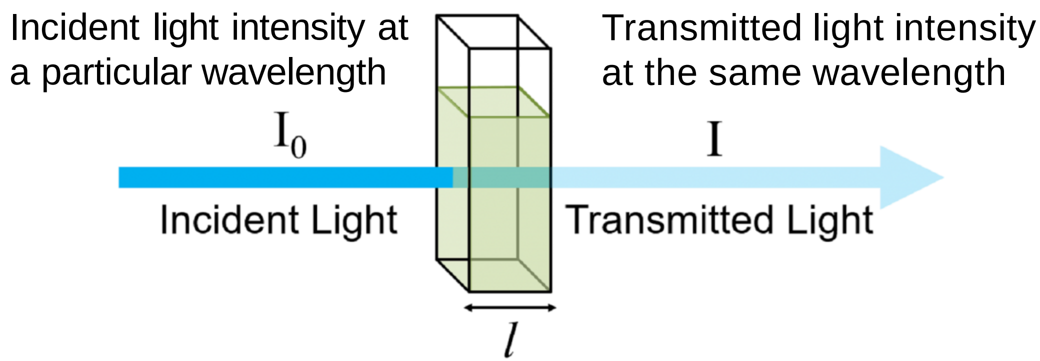
THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Lambert Beer's Law / Beer's Law

A brief outline:

- Introduction to absorption of light
- Definition and derivation of Lambert-Beer's Law / Beer's Law
- Relationship between absorbance and transmittance
- A plot of transmittance and absorbance vs sample concentration
- Properties and units of molar absorption coefficient
- Application of Beer's Law
- Limitations of Beer's Law

Absorption of Light



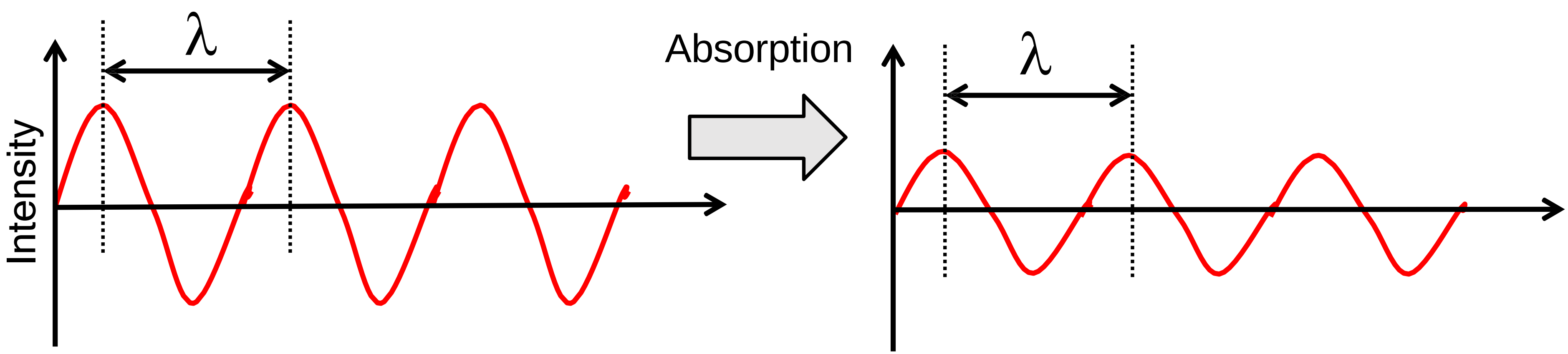
- If the sample does not absorb the incident light

  $I = I_0$

- If the sample absorbs the incident light

  $I \neq I_0;\ I < I_0$

Recall: Intensity = |Amplitude|^2

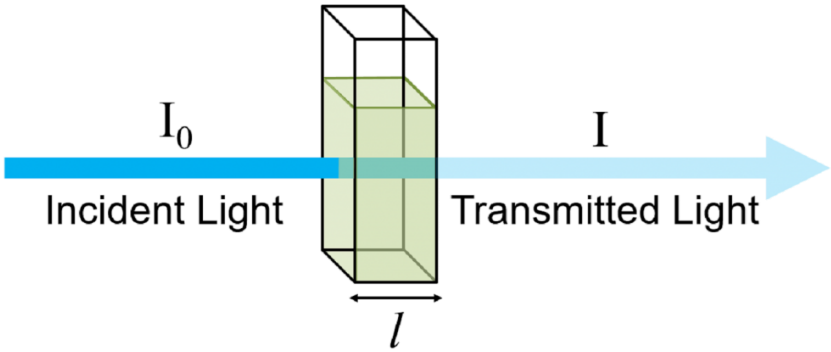


Note:

Transmitted intensity decreases with respect to the Incident intensity

Wavelength remains constant or unchanged upon absorption

Lambert-Beer's Law / Beer's Law



$$\boxed{A = \varepsilon\, c\, l}$$

A= absorbance

ε = molar absorption coefficient

c = concentration

l = path length

Definition of Lambert-Beer's Law / Beer's Law

When a beam of monochromatic radiation passes through a dilute solution of an absorbing substance, then the rate of decrease of intensity of radiation with the thickness of the absorbing medium is directly proportional to the intensity of incident radiations and concentration of the solution.

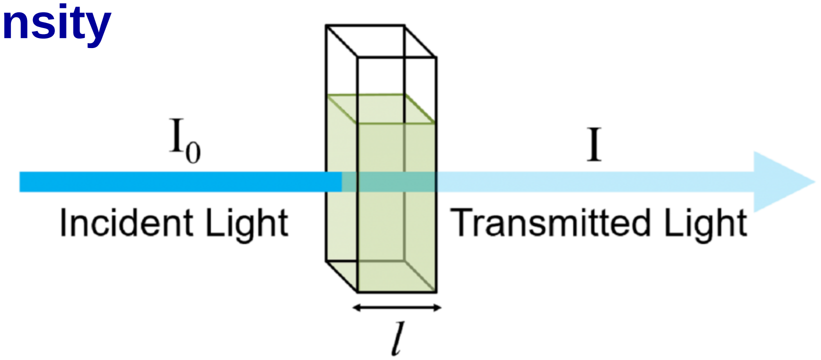
(OR)

The intensity of a beam of monochromatic radiations decreases exponentially with an increase in the thickness and the concentration of the dilute absorbing solution

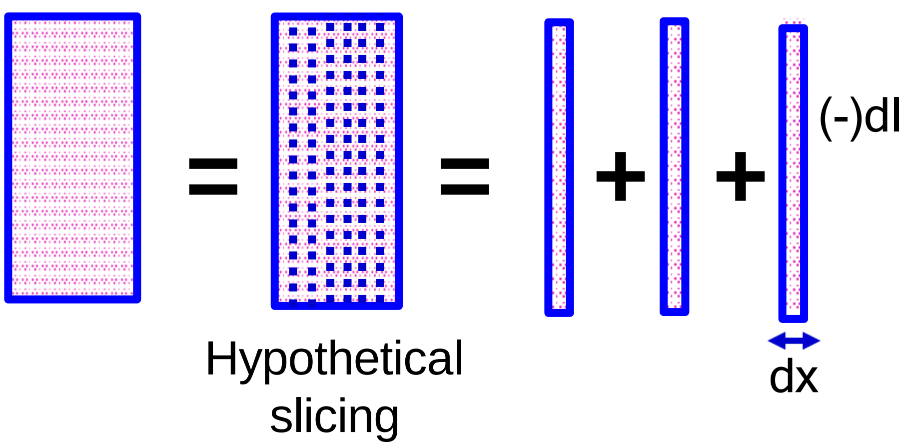
Derivation of Lambert-Beer's / Beer's Law

Factors Affecting the Transmitted Light Intensity

- ❖ Thickness of sample/Path length
- ❖ Concentration of Sample/Analyte



Let I_0 and I be the intensity of incident and transmitted radiation, respectively, x be the thickness, and **c** be the concentration of the solution



where (-)**dI** is the change in intensity upon absorption of incident radiation on passing through a thickness **dx** of the solution

Derivation of Lambert-Beer's / Beer's Law

$$-\frac{dI}{dx} \propto cI \quad \Rightarrow \quad -\frac{dI}{dx} = KcI \quad \Rightarrow \quad -\frac{dI}{I} = Kcdx$$

'K': proportionality constant.

Note: The minus sign is introduced because there is a reduction in the intensity upon absorption

Integrating the equation between limit I = I_0 at x = 0 and I = I at x = l we get,

$$\int_{I_0}^{I} -\frac{dI}{I} = Kc\int_{x=0}^{x=l} dx$$

$$\Rightarrow \ln\frac{I}{I_0} = -Kcl$$

$$\Rightarrow \ln\frac{I_0}{I} = Kcl$$

$$\Rightarrow 2.303\log_{10}\frac{I_0}{I} = Kcl$$

$$\Rightarrow \log_{10}\frac{I_0}{I} = \left(\frac{K}{2.303}\right)cl$$

$$\Rightarrow \boxed{\log_{10}\frac{I_0}{I} = \varepsilon cl} \left(as\ \frac{K}{2.303} = \varepsilon\right)$$

$$\boxed{\text{Absorbance (A)} = \log_{10}\frac{I_0}{I}} \left(\text{where, } \log_{10}\frac{I_0}{I} = \varepsilon cl\right)$$

$$\Rightarrow \boxed{A = \varepsilon cl}$$ ***Lambert Beer's Law eqn.***

where, A = Absorbance
ε = Molar absorption coefficient
c = Concentration of the sample/analyte
l = Path-length of the solution

Based on these equations, we can also write

$$\boxed{\text{Transmittance (T)} = \frac{I}{I_0}} \left(\text{where, } \frac{I}{I_0} = e^{-Kcl}\right)$$

Relationship between Absorbance and Transmittance

As we already know; $\mathrm{T} = \dfrac{I}{I_0}$ and $\mathrm{A} = \log_{10}\dfrac{I_0}{I}$

Hence, we may write: $\mathrm{A} = \log_{10}\dfrac{1}{\frac{I}{I_0}} = \log_{10}\dfrac{1}{T} = -\log_{10}T \Rightarrow \mathrm{T} = 10^{\text{-A}} = 10^{\text{-}\varepsilon\text{cl}}$

If Transmittance is expressed in percentage as $\%\mathrm{T} = \mathrm{T} \times 100 \Rightarrow \mathrm{T} = \dfrac{\%T}{100}$

Hence, we may rewrite the eqn. $A = \log_{10}\dfrac{1}{T}$ as: $\mathrm{A} = \log_{10}\dfrac{1}{\frac{\%T}{100}} = \log_{10}100 - \log_{10}\%\mathrm{T}$

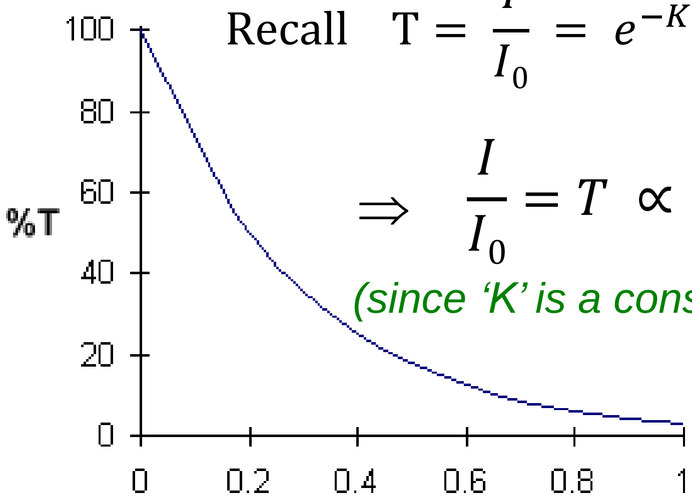
or, $\mathrm{A} = 2 - \log_{10}\%\mathrm{T}$

Relationship between Absorbance and Transmittance vs concentration

Recall $\mathrm{T} = \dfrac{I}{I_0} = e^{-Kcl}$

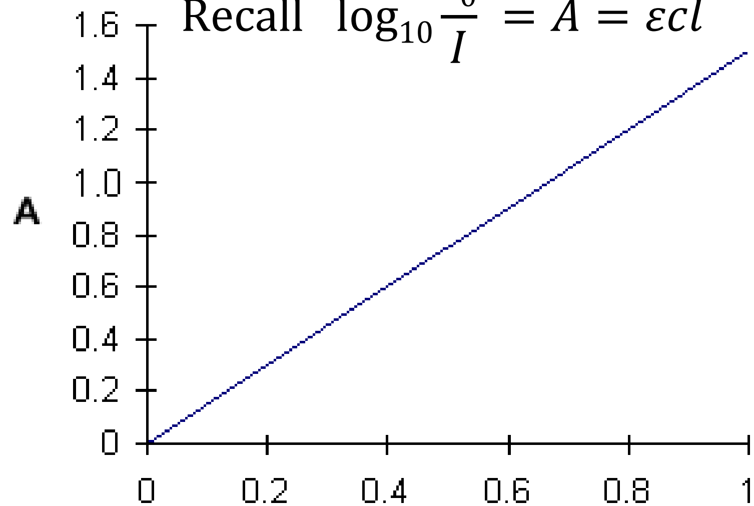
$\Rightarrow \dfrac{I}{I_0} = T \propto e^{-cl}$

(since 'K' is a constant)



Concentration

Recall $\log_{10}\dfrac{I_0}{I} = A = \varepsilon cl$



Concentration

Key-points for Solving Beer's Law Numericals

As we already know; $T = \dfrac{I}{I_0}$ and $A = \log_{10}\dfrac{I_0}{I}$

Conversion (Numericals) ⟷ **Represents double-headed arrow (e.g. Two-way traffic)**

(Transmittance) T ⟷ % T **(Percent Transmittance)**

(%T = 100 x T)

(Applicable)

($A = -\log_{10}T$)
or,
($T = 10^{-A}$)

(Applicable)

(%A = 100 - %T)

(Applicable)

A **(Absorbance)**

% A' **(Percent Absorption)**

(Not Applicable)

To calculate %A' from A
Take a detour via
A → T → %T → %A'

Properties and Units of Molar Absorption Coefficient

1. Units of Molar absorption coefficient

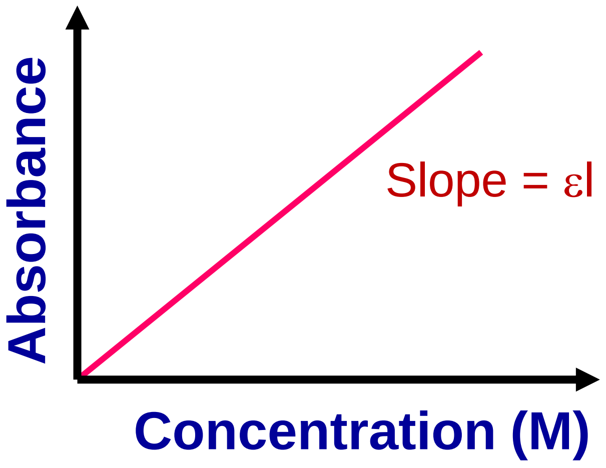
$$A = \varepsilon c l \Rightarrow \varepsilon = {}^{A}\!/_{cl}$$

According to convention; the unit of c is Molar (M) = mol/L = mol/dm^3
the unit of l is a centimeter (cm)
and Absorbance is a dimensionless quantity

The units of ε is = $M^{-1}cm^{-1}$ = $Lmol^{-1}cm^{-1}$ = $dm^3mol^{-l}cm^{-l}$ = cm^2mol^{-l}

2. Properties of Molar absorption coefficient

- ❖ Constant
- ❖ Molecule-specific
- ❖ Wavelength-dependent

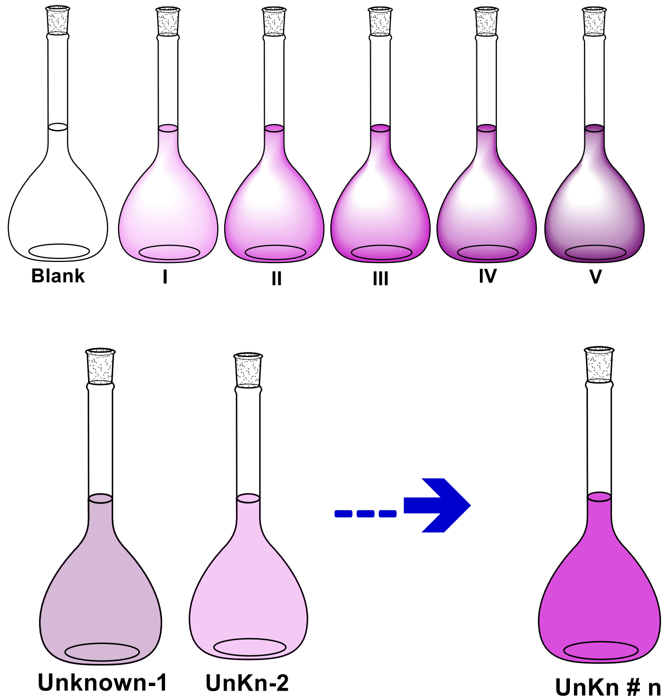


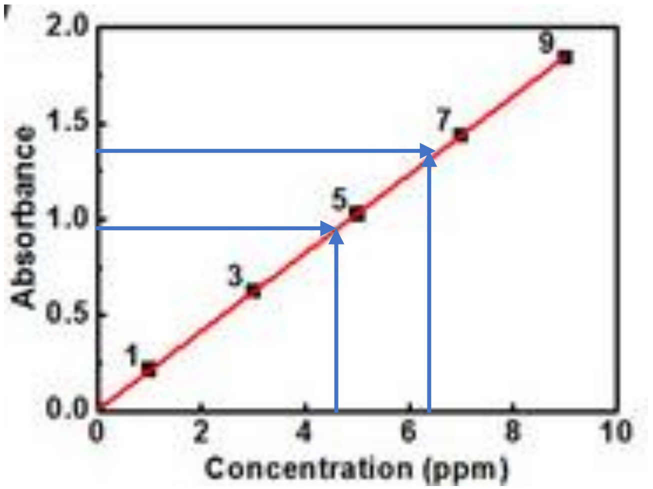
How do we use Beer-Lambert Law ?

1. Numerical

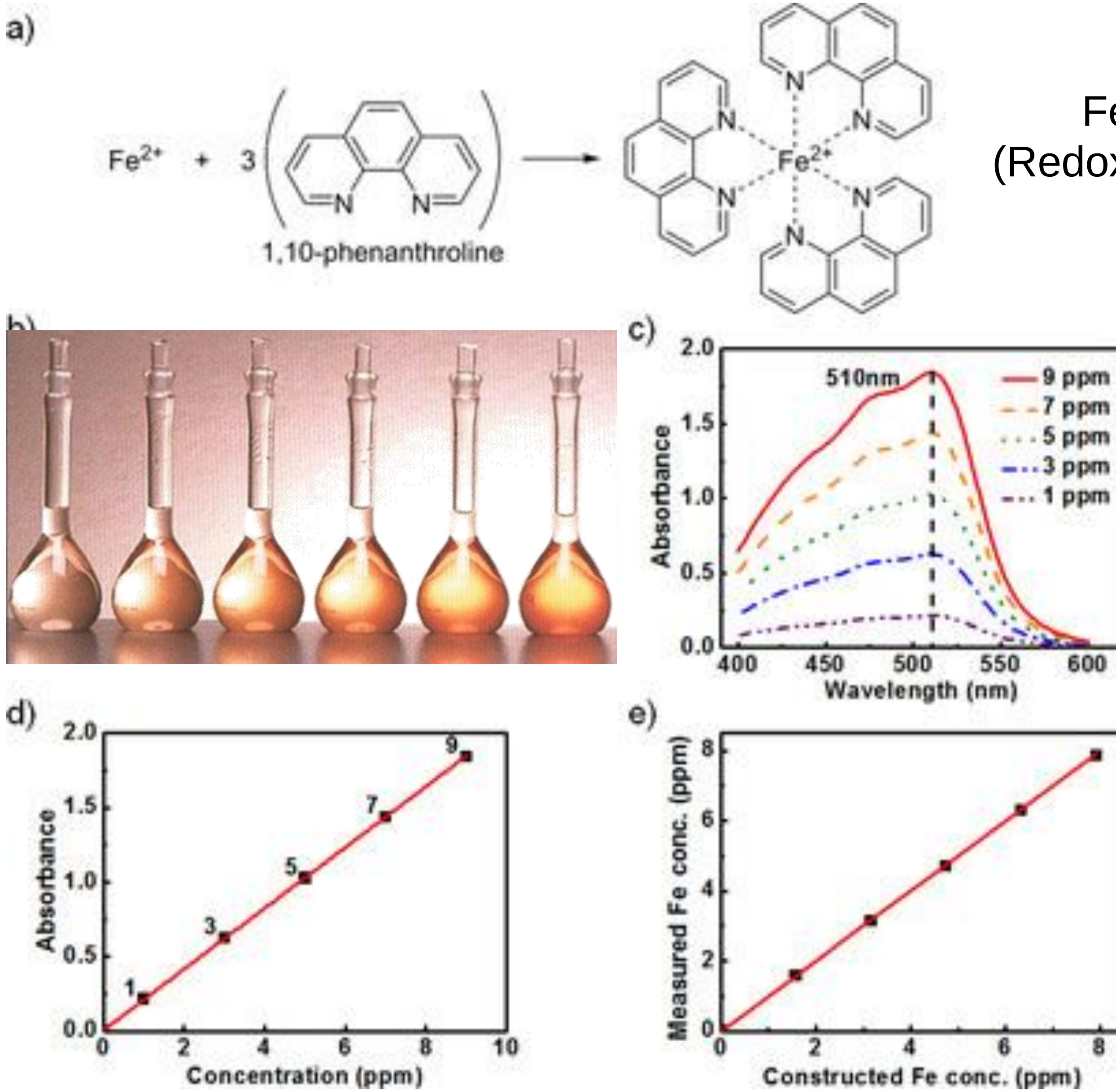
A monochromatic radiation is incident on a solution of 0.05 molar concentration of an absorbing substance. The intensity of the radiation is reduced to one fourth of the initial value after passing through 10 cm length of the solution. Calculate the molar extinction coefficient of the substance……....

2. Finding the unknown **$A = \varepsilon cl$**





Lambert-Beer Law: Proof-of-concept experiment in Chemistry Lab



Ferroin
(Redox indicator)

Augustina et al. ChemistryOpen 2015; DOI: 10.1002/open.201500096

Limitations of Lambert-Beer Law

- Beer's law is applicable to dilute solutions only
- The radiation should be monochromatic
- Solute must not undergo association, dissociation, polymerization, or hydrolysis in the solvent

1. State Lambert-Beer's law. What do you mean by absorbance and transmittance?
2. What are the units used for the Molar Extinction Coefficient?
3. The molar extinction coefficient of $Coen_2Br^{2+}$ is 40 M^{-1} cm^{-1} at 650 mμ (milli micron). Calculate the percent transmission for a 5 cm cell filled with 0.01 M solution. What will be the corresponding absorbance?
4. A 0.003 M solution of $[Co\ (NH_3)_6]^{3+}$ transmits 75% of incident light of 500 mμ if the path length is 1 cm. Calculate the molar extinction coefficient and the percent absorption for a 0.01 M solution.
5. A substance in an aqueous solution at a concentration of 10^{-3} M absorbs 10% of incident light in a path length of 1 cm. What concentration will be required to absorb 90% of the light?
6. At 460 nm, a blue filter transmits 72.7% of the light, and a yellow filter transmits 40.7% of the light. What is the transmittance at the same wavelength of two filters in combination?